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MELPAR, INC.

The Detection of Oxygen by Gas-Phase Polarography at Low Temperatures and Low Pressures

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INTRODUCTION

The detection of oxygen has been widely accomplished by various electroanalytical and chemical methods. This paper describes an oxygen detector which involves the principle of gas-phase polarography. Oxygen detectors of this type are already in existence; the particular type discussed here, however, has an additional capability of operating at low temperatures (to -25°C) and low pressures (10 mm Hg). The sensitivity range is from 0.001% to 100% oxygen.

In gas-phase polarography,[1] as in conventional solution polarography, the cell contains a polarized microelectrode and a reversible reference electrode in a suitable electrolyte. In gas-phase polarography, as distinguished from conventional polarography, however, the diffusion layer is contained by a membrane which is held taut against the microelectrode. In this particular polarographic oxygen detector, the gas mixture diffuses through the special semipermeable membrane and dissolves in the electrolyte. Oxygen in the electrolyte is electrochemically reduced at the polarized cathode in the ususal polarographic sense. Except for the membrane-diffusion process, gas-phase polarography is similar to ordinary polarography.

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EXPERIMENTAL

Cell Construction and Assembly

The test cell shown in figure 1 is constructed with the use of special glass O-ring seals.[a] The polarized microelectrode is a platinum inlay.[b] Pretreatment of this electrode is accomplished by electroreduction for 5-10 seconds at 22.5 vdc in HCl solution containing a small amount of detergent. The reference electrode is of silver-silver chloride, made from silver wire spirally wound around the platinum-inlay electrode. The membrane is 0.5-mil Teflon.[c] The electrolytes are prepared with certified reagent-grade chemicals. During initial work, saturated KCl was used, but for work at -25°C, an alcoholic solution of potassium chloride is required. The solution chosen consists of 24% methanol (by weight), 5% KCl, and 71% H_2O. A phosphate buffer is added to maintain the pH at 6. The screen is an electroformed grid made of 40-mesh stainless steel.[d]

The cell is assembled as follows.

1. The membrane and screen are set between glass O-ring connectors, using Viton-O-rings.

2. The cell container is half filled with electrolyte and N_2 is bubbled through the cell for 10 minutes to eliminate oxygen in the electrolyte.

3. The electrodes are fixed in a rubber stopper and, after pretreatment, inserted into a cell so that the platinum microelectrode is pressed firmly against the membrane.

4. The cell is now ready for calibration. The test gases are nitrogen,[e] air, and calibrated mixtures of 1%, 0.1%, and 0.001% oxygen in prepurified nitrogen.[f]

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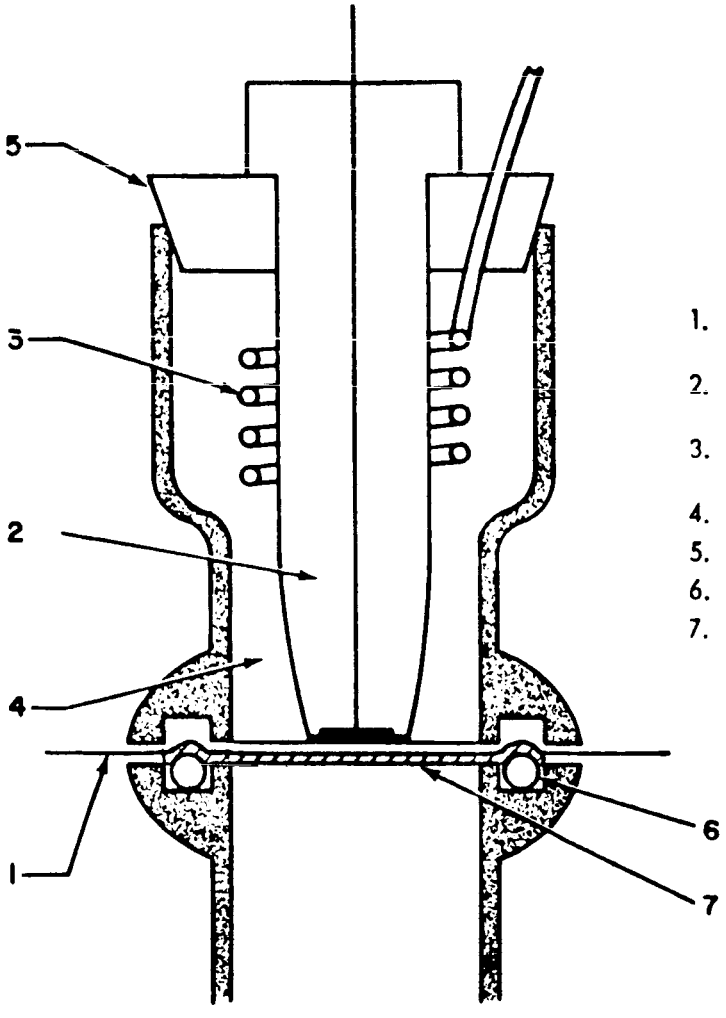
[a] From Konte's Glass Co., Vineland, N. J.
[b] Beckman Electrode Catalog No. 39273.
[c] E. I. du Pont and Co., Wilmington, Delaware.
[d] Jelliff Co., Baltimore, Md.
[e] Seaford grade.
[f] [illegible] The Matheson Company, Inc., East Rutherford, New Jersey.



1. 0.5 MIL TEFLON MEMBRANE
2. PLATINUM INLAY ELECTRODE
3. SILVER-SILVER CHLORIDE REFERENCE ELECTRODE
4. ELECTROLYTE
5. NEOPRENE STOPPER
6. VITON - O RING
7. SCREEN

Figure 1. Schematic of Cell

Polarographic Measurements

The polarographic measurements are made with a Leeds and Northrup Electrochemograph or a Fisher Scientific Co. Elecdropode. Because the measurements are made in unstirred solutions, the desired potential is applied to the cell, followed by a two-minute wait, before the current data is taken. For the low oxygen concentrations which give a very low current output, a circuit has been devised which essentially uses an ordinary dry cell with a voltage divider for applying potential and a galvanometer[g] with a sensitivity of 0.0004 μa/div for current measurement. The schematic diagram is shown in figure 2.

Membrane Study

The method of gas-phase polarography requires that the semi-permeable membrane be stretched tightly across the platinum electrode surface so that only a thin film of electrolyte separates the electrode from the interstices of the membrane. Diffusion of the gas containing molecular oxygen occurs through the membrane to the electrolyte. The significant properties of the membrane are: high oxygen permeability, yet insignificant porosity; high and low temperature stability; and physical strength.

High oxygen permeability is obviously desired to achieve maximum sensitivity. The membrane must be permeable to oxygen, but not so porous that the electrolyte leaks out. A fine distinction exists between permeability and porosity because of the difficulty to determine where one begins and the other ends. In the experimentation, however, this becomes obvious.

The membrane is required to maintain its characteristic permeability at low temperatures (to -25°C) without adverse effect. Also, in accordance with the particular application, the membrane must be capable of withstanding a temperature of 145°C for 24 hours.

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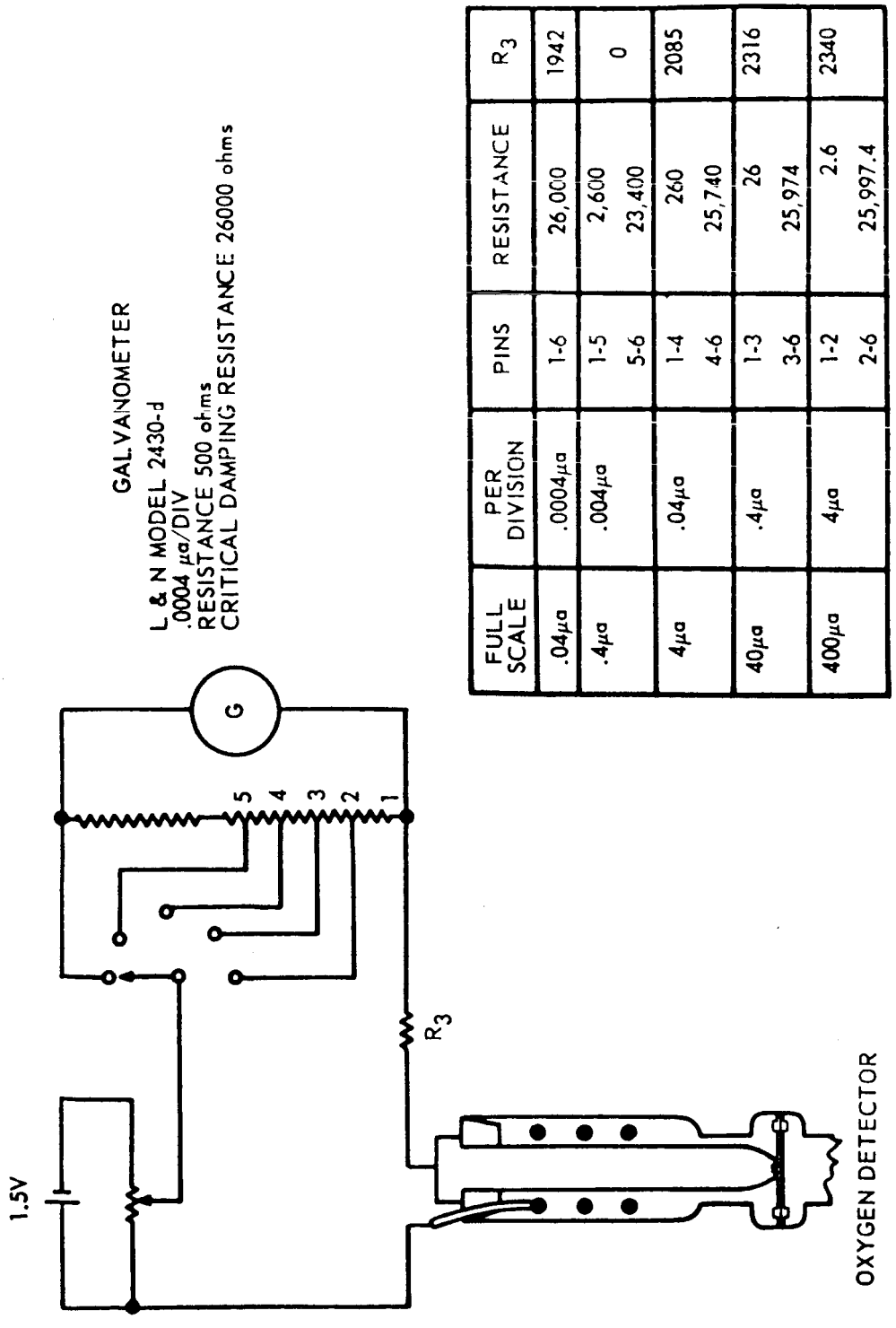
[g] The Mathieson Company, Inc., East Rutherford, New Jersey. Leeds and Northrup No. 2430-d.



FULL SCALE	PER DIVISION	PINS	RESISTANCE	R_3
.04μa	.0004μa	1-6	26,000	1942
.4μa	.004μa	1-5	2,600	0
		5-6	23,400	
4μa	.04μa	1-4	260	2085
		4-6	25,740	
40μa	.4μa	1-3	26	2316
		3-6	25,974	
400μa	4μa	1-2	2.6	2340
		2-6	25,997.4	

Figure 2. Circuit Schematic

Good physical strength, including burst and tear strength characteristics, is important because, while the oxygen detector operates at low pressures, the membrane must support greater than a 750-mm pressure differential.

From the many commercially available membranes, one with the specific characteristic of high oxygen permeability had to be chosen. More than 60 types have been tested. Included are: polyethylene from du Pont, Dow, and Visking Corp.; Teflon from du Pont; silicone rubber from Norris Manufacturing Co. and Materials Testing, Inc.; and cellophane, gum rubber, various silicone-coated fabrics, Saran, fibrous mixtures, "microporous" membranes, nylon, neoprene, Visqueen, Trycite, Trithene, Tedlar, and cellulose acetate from various manufacturers. Three of these have desirable properties: polyethylene, Teflon, and silicone rubber. The tests confirm results reported in the literature.[2] Obtaining the best sensitivity is desirable, and because permeability is approximately a linear function of membrane thickness, only very thin membranes have been considered.

A polyethylene membrane (0.001 inch thick) has proved to be too weak structurally; silicone rubber has given nonreproducible results, attributable to its attack slowly by KCl.[3]

Teflon, in the form of a 0.5-mil-thick membrane, has exhibited sufficient strength and oxygen permeability and possesses the desired temperature characteristics.

RESULTS AND DISCUSSION

The reduction of oxygen at a microelectrode in neutral solution occurs by the following reaction:

$$\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

The half-wave potential vs. a saturated calomel electrode is reported to occur at 0.16 to 0.20 volt, in solution, and the reduction wave is independent of pH for a prereduced or unconditioned electrode.[4]

A polarographic wave, utilizing the 0.5-mil Teflon membrane with saturated KCl electrolyte under atmospheric pressure and at room temperature, is shown in figure 3. The half-wave potential is 0.16 volt and the diffusion current 15.0 μa for this typical gas polarographic wave of oxygen. From this starting point, the capability of the polarographic oxygen detector has been extended to the regions of low pressure and low temperature. Experiments have been conducted to measure oxygen concentrations in gases at pressures down to 10 mm Hg and/or at temperatures as low as -25°C.

For low-pressure application, a screen is inserted beneath the membrane to prevent it from bulging outward and tearing. The screen, fabricated by electroforming techniques, eliminates rough edges which could cause tearing. The Teflon membrane offers an advantage of good tear and burst strength, even at the 0.5-mil thickness.

The diffusion-limited current, under atmospheric pressure and at room temperature, has always been in the range of -0.6 to -0.8 volt, applied between the silver-silver chloride reversible electrode and the platinum-inlay electrode. Thus, it has been decided to work in this range during the entire experimental program.

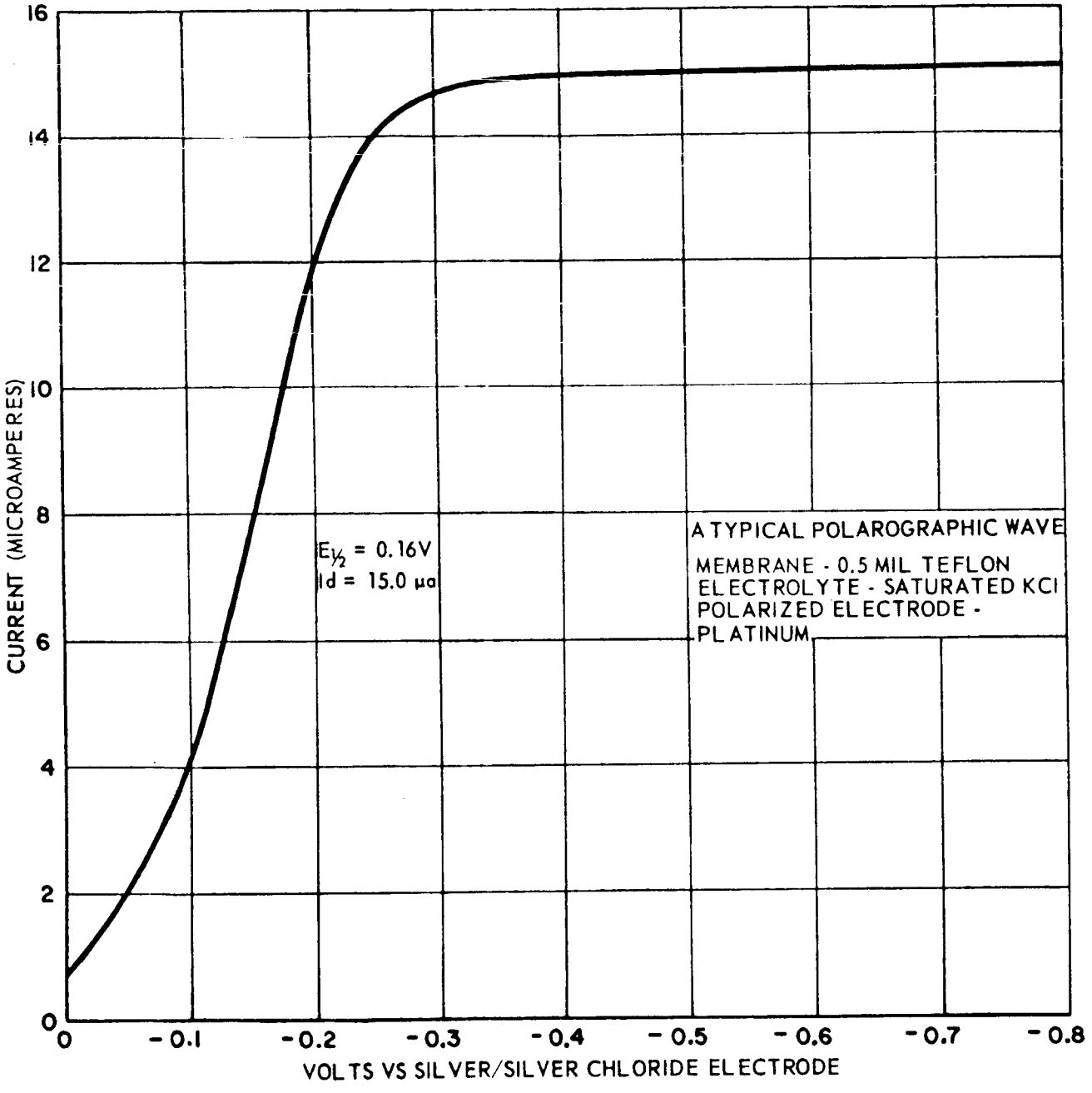


Figure 3. Typical Polarographic Wave

Experiments that indicate sensitivities at low concentrations are shown in figure 4. Difficulty exists from not obtaining a suitable current background. This is because Seaford nitrogen and prepurified grades of nitrogen contain less than 0.002% oxygen as impurity.[h] As shown in figure 4, the sensitivity deviates slightly as one changes from 0.6 to 0.8 volt. The current readings, however, are linear to as low as 0.01% oxygen, where slight deviation occurs. The mixtures for these experiments have been calibrated; thus, it is possible to estimate the oxygen concentrations in the Seaford nitrogen gas from the calibration curve of the detector.

For O_2 determinations in which the temperature of the gas is below the freezing point of ordinary aqueous electrolytes, such as KCl solutions, a modification in electrolyte composition is required. This problem has been given considerable attention. Polarography of dissolved gases has been performed using $CaCl_2$ and LiCl in absolute alcohols.[5] Various salt-solvent mixtures have been investigated in the laboratory. These include: KCl-glycol, KCl-glycol-water, LiCl-glycol-water, LiCl-methanol, LiCl-methanol-water, $CaCl_2$-methanol-water, KC-methanol-water, and KC-ethanol-water. A mixture, found to be suitable for detection in the gas phase for this oxygen detector, consists (by weight) of 24% methanol, 71% water, and 5% KCl. The freezing point of this mixture is approximately -27°C. Figure 5 shows the results of temperature runs of the gaseous oxygen mixture at 26°, 0°, and -20°C. As can be seen, there is a reduction in sensitivity; even with this reduction, however, a distinguishable current measurement at the low temperature is observed.

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[h] Manufacturer's specifications.

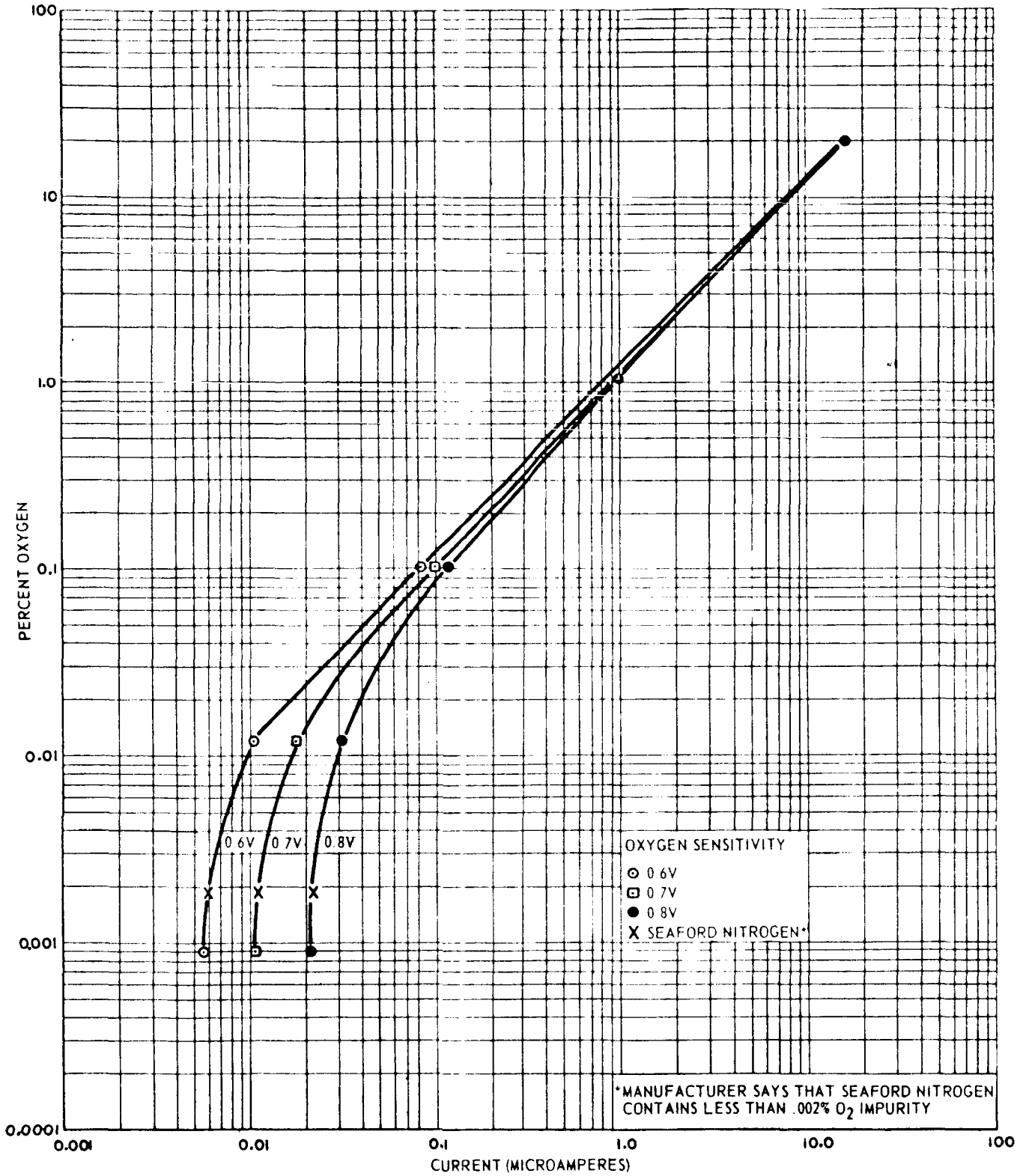

Figure 4. Sensitivity

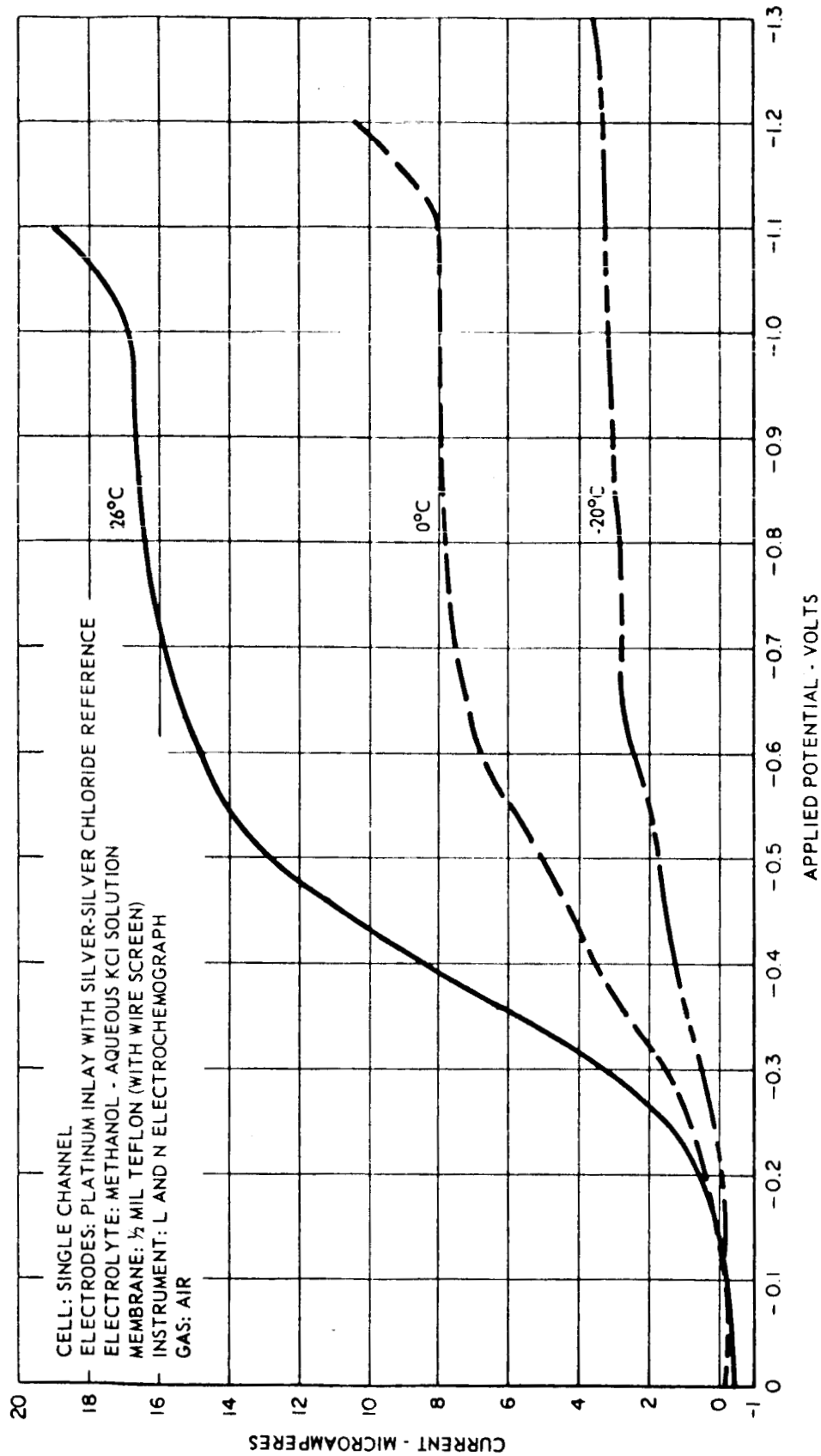

Figure 5. Temperature Sensitivity

Although the oxygen detector is capable of working at low temperatures, the variation in temperature while monitoring must be considered. To reduce the effects caused by temperature variation, a thermistor circuit can be employed.[6]

The sensitivity at low pressures is determined by filling the sample chamber with the desired gas concentration and evacuating to the desired pressure. Current readings have been observed as low as 1 mm of Hg but, in this lower-pressure range, have not been highly reliable. Figure 6 gives the results obtained while working at low pressures. A linear relationship is observed over the range of 1 - 76 mm Hg. The data have been taken by going from vacuum to increased pressure, and then from pressure to vacuum. Thus, any possible hysterisis effects are operative. None has been observed. These results are significant because the electrolyte and inner parts of the cell are under one atmosphere of pressure, while the outer side of the membrane is subjected to the reduced pressures.

Certain studies of interferences have been made. Nitrogen and argon, as expected, have no effect. One percent of CO_2 in nitrogen has a slight effect, but 0.1% of CO_2 causes no deviation. The effect of ozone as an interfering species has been investigated. Ozone is generated by an apparatus similar to that described by Hughes.[7] Only large concentrations of 0.1% ozone are detected, and this affects the readings only slightly.

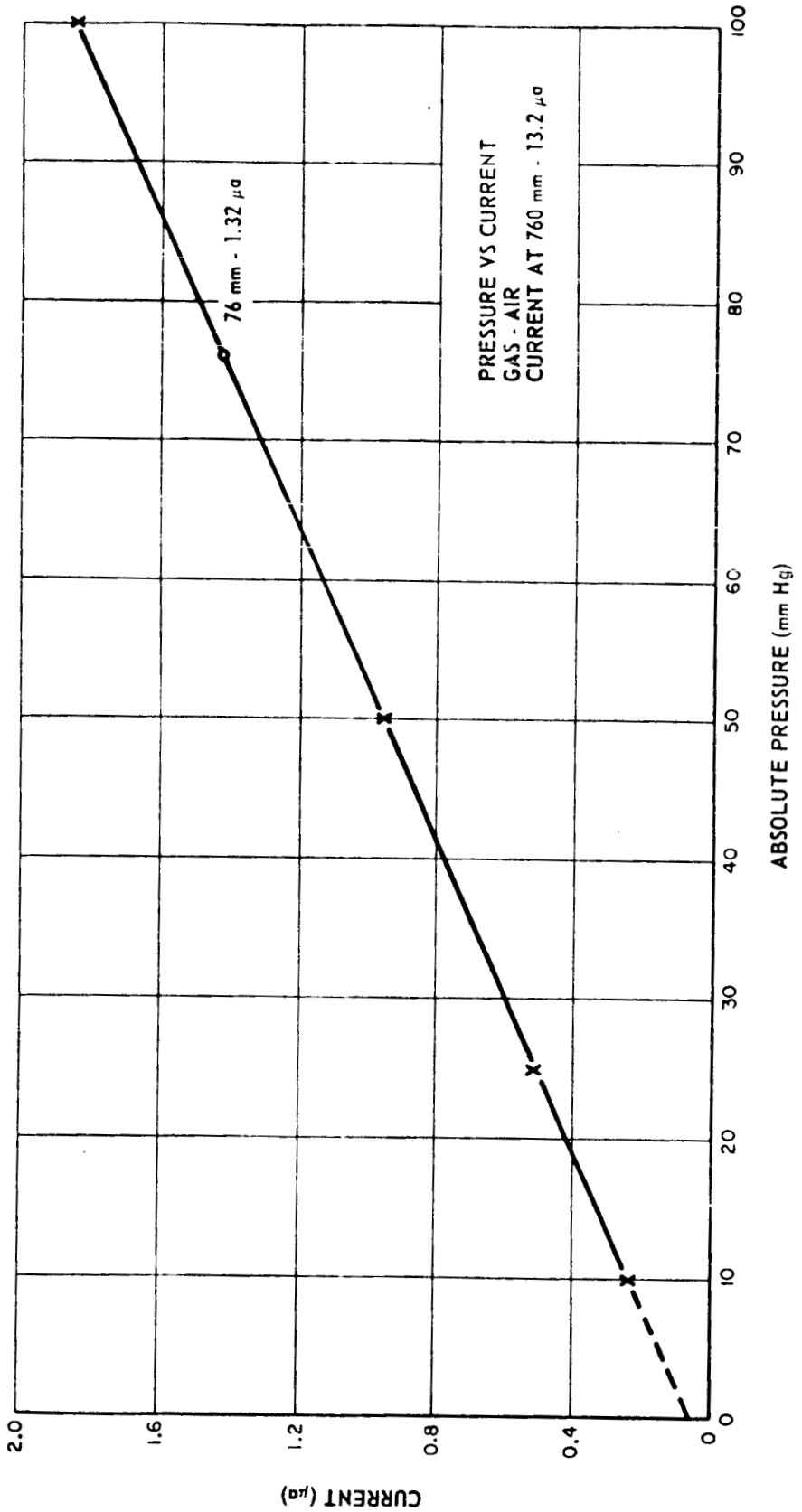

Figure 6. Sensitivity at Low Pressure

ACKNOWLEDGMENTS

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